

Synthesis and Thermal Properties of Poly(urethane-imide)

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ABSTRACT: The synthesis and thermal properties of thermoplastic poly(urethane-imide) (PUI) resins were studied. Model reaction studies on the reactions of 4,4'-diphenylcarbamatodiphenylmethane and 4,4'-diisocyanatodiphenylmethane with phthalic anhydride were performed. We found that the reaction of anhydrides with urethane groups could take place under certain reaction conditions. According to the model reaction studies, *N*-2-methylpyrrolidone was employed as a solvent, and no catalyst was used in the polymerization. To restrain the side reaction of anhydrides with urethane groups, we adopted a two-step chain-extending procedure in a chain-extending reaction. The inherent viscosity of PUI was 0.83–0.99 dL/g. The prepared polymers not only exhibited improved solubility in organic solvents but also formed flexible films. Thermogravimetric analysis showed that PUI exhibited a two-step thermal weight-loss pattern. The first step of the thermal degradation of PUI was attributed to the thermooxidizing cleavage of weak and labile linkage, such as urethane groups, isopropylidene, and methylene, except for imide rings. The polymer inherent viscosity decreased sharply during the first step of thermal degradation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 773–781, 2001

Key words: poly(urethane-imide); polyimide; polyurethane; thermal properties; thermogravimetric analysis

INTRODUCTION

Polyimides have been extensively used in many applications, including films, adhesives, varnishes, electronic packing materials, and matrix resins of advanced composites at elevated temperatures. However, solubility and processability are still a major concern in studies of polyimides. An effective approach for improving solubility and processability that has been successfully applied

is the introduction of flexible linkages, which come from either the diamine or the dianhydride component into the polyimide main chain. The flexible linkages include ether (—O—), sulfur (—S—), sulfone (—SO₂—), and isopropylidene [—C(CH₃)₂—], as well as hexafluoroisopropylidene [—C(CF₃)₂—].^{1–5} Another approach is the synthesis of copolyimides such as poly(amide-imide) and poly(ester-imide).^{6,7}

Our preliminary research on thermoset poly(urethane-imide) (PUI) has proven that bismaleimide with urethane linkages (BMIU) prepared from Diels–Alder reactions of bisfuranylmethylcarbamate and 4,4'-(bismaleimidodiphenyl) methane (BMI) is an effective modifying agent of the

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toughness of BMI.⁸ By directly mixing BMIU and BMI in different ratios, one can prepare a series of toughened bismaleimide resins. The toughened bismaleimide resins not only have relatively low softening points but also can dissolve in a mixture of acetone and ethylene glycol monomethyl ether to form homogeneous resin solutions with excellent storage stability. It is expected that the toughened bismaleimide resins can be used in composites, adhesives, and varnishes. There has been some research on the preparation of thermoplastic PUI. However, such polymers have exhibited brittleness due to their low inherent viscosity, with the exception of PUI elastomer prepared from polyether or polyester diol.^{9–17} The objectives of this research were the synthesis of thermoplastic PUI resins able to form tough and flexible films and the study of the solubility and thermal properties of the resulting polymers.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) was purified by recrystallization from acetic anhydride followed by sublimation. 2,2-Bis(4-hydroxyphenyl)propane (BHPP) was purified by recrystallization from toluene and then dried under reduced pressure at 50°C. Diethylene glycol (DEG) and 4,4'-diisocyanatodiphenylmethane (MDI) were purified by distillation under reduced pressure. *N*-2-Methylpyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc) were dried with CaH₂ for 24 h at first and then distilled under reduced pressure. Methanol, acetone, and ethanol were dried with CuSO₄. Hexane, toluene, dichloromethane (DCM), phthalic anhydride, and tetrahydrofuran (THF) were chemical reagents and were used as received.

Model Reaction Studies

Reaction of MDI with Phthalic Anhydride

MDI (5 g, 0.02 mol) was dissolved in NMP, and then phthalic anhydride (5.92 g, 0.04 mol) was added. The reaction mixture was maintained at a certain temperature for 12 h. Then, the mixture was poured into excess ethanol, and the resulting product 4,4'-(bisphthalimidodiphenyl)methane was filtered and washed three times with ethanol. The reaction in DMF and DMAc was performed similarly. In some cases, a trace of triethylamine, di-*n*-butyltin dilaurate, or water was used as a catalyst.

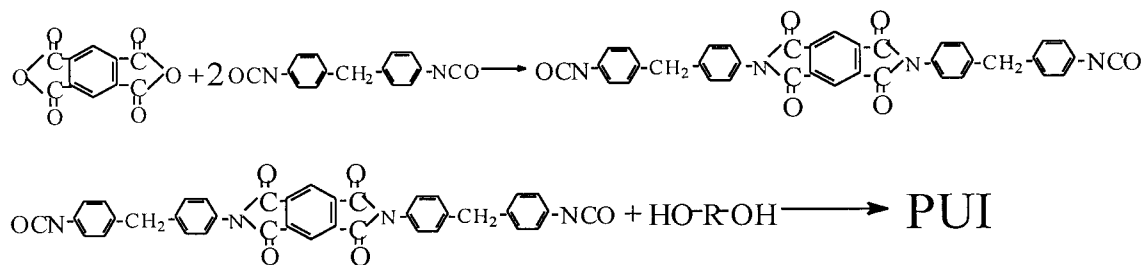
Reaction of 4,4'-Diphenylcarbamtodiphenylmethane with Phthalic Anhydride

4,4'-Diphenylcarbamtodiphenylmethane (4.38 g, 0.01 mol) prepared from the reaction of phenol and MDI was dissolved in NMP, and then phthalic anhydride (2.96 g, 0.02 mol) was added. The mixture was maintained at a certain temperature for 12 h. Then, the mixture was poured into excess ethanol, and the resulting product was washed three times with acetone. In some cases, water was used as a catalyst.

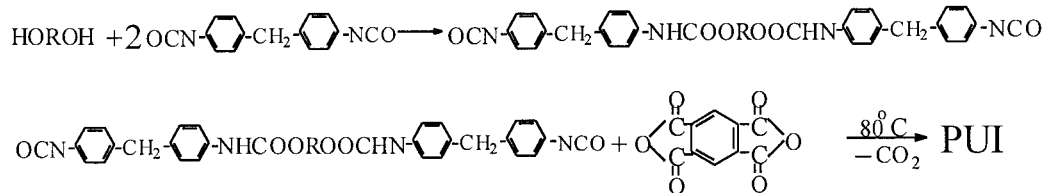
Synthetic Procedures

Typical Synthetic Procedure of PUI from NCO-Terminated Polyimide Prepolymer

PMDA (2.18 g, 0.01 mol dissolved in 12 g of NMP) and MDI (5 g, 0.02 mol dissolved in 28 g of NMP) were added to a 250-mL, three-necked flask equipped with a constant flow of dried nitrogen, a thermometer, a thermostat, and a stirrer. The reaction was carried out at 100 ± 1°C, and the beginning of the reaction was observed through the evolution of carbon dioxide. After a certain period of time, the temperature was decreased to 80°C, and a dihydric compound (0.01 mol in NMP)



Scheme 1 Synthetic reaction of PUI from polyimide prepolymer.



Scheme 2 Synthetic reaction of PUI from polyurethane prepolymer.

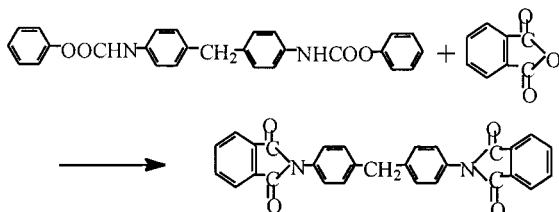
was added dropwise to the NCO-terminated polyimide prepolymer over a period of 30 min. After the chain-extending reaction, the polymerization mixture was poured into excess methanol, and the resulting polymer was filtered and dried under reduced pressure at 50°C (Scheme 1).

Typical Synthetic Procedure of PUI from NCO-Terminated Polyurethane Prepolymer

MDI (5 g, 0.02 mol dissolved in 28 g of NMP) and a dihydroxylic compound (0.01 mol dissolved in NMP) were added to a 250-mL, three-necked flask equipped with a constant flow of dried nitrogen, a thermometer, a thermostat, and a stirrer. The reaction was carried out at $80 \pm 1^\circ\text{C}$. After a certain period of time, PMDA (2.18 g, 0.01 mol dissolved in 12 g of NMP) was added dropwise to the NCO-terminated polyurethane prepolymer over a period of 30 min. After the chain-extending reaction, the polymerization mixture was poured into excess methanol, and the resulting polymer was filtered and dried under reduced pressure at 50°C (Scheme 2).

Measurement

The IR spectrum was recorded on a Nicolet 20-SXB Fourier transform infrared (FTIR) spectrometer. Elemental analysis was performed with a Carlo Erba 1106-type elemental analysis instrument. Thermogravimetric analysis (TGA) was carried out with a PE-7 thermal analysis system



Scheme 3 Model reaction of 4,4'-diphenylcarbamotodiphenylmethane and phthalic anhydride.

under an air atmosphere at a heating rate of 10°C/min.

The polymer inherent viscosity was measured with a Ubbelohde viscosity meter with a polymer solution of 0.5 g of PUI in 100 mL of DMAc at 25°C.

RESULTS AND DISCUSSION

Model Reaction Studies

Before the polymer syntheses, model reaction studies on the reaction of MDI with phthalic anhydride were carried out briefly. The results were similar to those reported in the literature.¹⁷ In summary, NMP was the best solvent among NMP, DMF, and DMAc for higher product yields and reaction speeds. The optimum reaction temperature was within 80–100°C. The introduction of a trace catalyst such as triethylamine or di-*n*-butyltin dilaurate apparently decreased the prod-

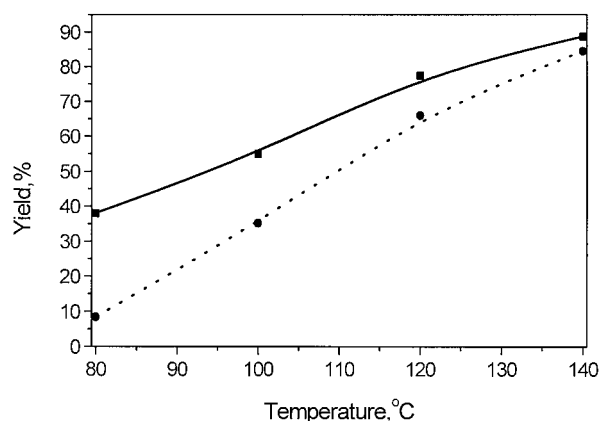


Figure 1 Effects of the temperature and water on the reaction of diphenylcarbamotodiphenylmethane and phthalic anhydride: (---) no water and (—) $[\text{H}_2\text{O}]/[\text{phthalic anhydride}] = 1/10$ mol/mol (reaction time = 12 h, $[\text{diphenylcarbamotodiphenylmethane}]/[\text{phthalic anhydride}] = 1/1$).

Table I Effect of Prepolymerization Time on the Inherent Viscosity of Poly(urethane-imide)

	Time (h)	Unreacted Isocyanate (%)	Inherent Viscosity (dl/g)	Film Properties
PUI from polyurethane prepolymer, prepolymerization at 80°C	0.5	64.3	0.18	Brittle
	1.0	51.2	0.31	Brittle
	1.5	50.2	0.46	Brittle
	2.0	49.3	0.48	Brittle
	2.5	43.2	0.24	Brittle
PUI from polyimide prepolymer, prepolymerization at 100°C	1.5	68.3	0.11	Brittle
	2.0	62.6	0.23	Brittle
	2.5	56.7	0.28	Brittle
	3.0	50.2	0.37	Brittle
	3.5	49.7	0.37	Brittle
	4.0	49.4	0.36	Brittle

Chain-extending reaction at 80°C for 20 h, (MDI/BHPP/PMDA = 2/1/1).

uct yield. On the contrary, the introduction of water increased the product yield. Besides the studies on the reaction of anhydrides with isocyanate compounds, some research has been done on the reaction of anhydrides with carbamate compounds. To obtain a full understanding of the PUI synthesis reaction, we studied the model reaction of phthalic anhydride with 4,4'-diphenylcarbamodiphenylmethane prepared from MDI with phenol. IR, mass, and $^1\text{H-NMR}$ spectrometry, melting-point detection, elemental analysis, and thermogravimetric experiments were used to characterize the resulting product. All these char-

acterizations identified the product as 4,4'-(bisphthalimidodiphenyl)methane, so the reaction can be expressed as in Scheme 3. Figure 1 shows that the yields depended on the reaction temperature under the conditions employed; the introduction of water increased the yields of the reaction, especially in the low-temperature range. A further experiment also proved a similar reaction of phthalic anhydride with 4,4'-diethylcarbamodiphenylmethane prepared from ethanol and MDI. However, the yield of the resulting product, 4,4'-(bisphthalimidodiphenyl)methane, was very low. This implies that the reaction of anhydrides with all-aromatic urethane groups could take place somewhat more easily than that of anhydrides with aromatic-aliphatic groups. The differences between all-aromatic urethane groups and aromatic-aliphatic groups should derive from their different stabilities with respect to heat and chemical reagents. Because the reaction of anhydrides with urethane groups is a side reaction in PUI synthesis, the reaction and its dependence on temperature must be taken into consideration in the preparation of PUI.

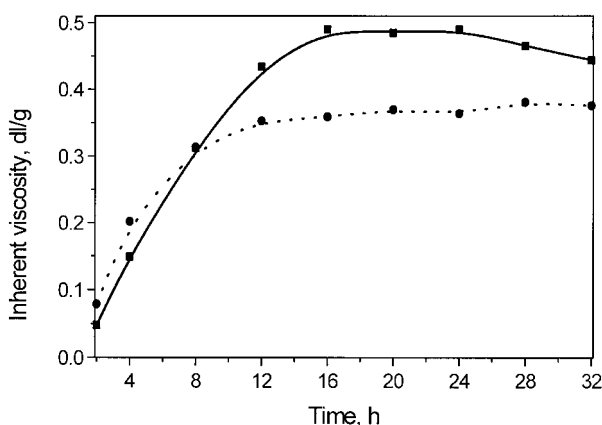


Figure 2 Effect of the chain-extending reaction time on the polymer inherent viscosity: (—) from polyimide prepolymer with the prepolymerization at 100°C for 3 h and (—) from polyurethane prepolymer with the prepolymerization at 80°C for 2 h (chain-extending reaction at 80°C, [MDI]/[PMDA]/[BHPP] = 2/1/1).

Synthesis of PUI

From the model reaction studies, NMP was employed as a solvent, and no catalyst was used in the following polymerization experiment. Table I and Figure 2 show the effects of the prepolymerization time and chain-extending reaction time on the inherent viscosity of the polymers synthesized according to Schemes 1 and 2, respectively. According to Table I, the optimum prepolymeriza-

Table II Effect of Chain-Extending Reaction Procedure on the Inherent Viscosity of PUI from Polyurethane Prepolymer

At Room Temperature (h)	At 80°C (h)	Inherent Viscosity (dL/g)		Film Properties	
		PUI-A	PUI-B	PUI-A	PUI-B
0	24	0.52	0.70	Brittle	Flexible
1	23	0.70	0.89	Flexible	Flexible
2	22	0.78	0.95	Flexible	Flexible
3	21	0.84	0.98	Flexible	Flexible
4	20	0.86	0.98	Flexible	Flexible
5	19	0.85	0.99	Flexible	Flexible

PUI-A: Prepolymerization at 80°C for 2.0 h, MDI/BHPP/PMDA = 2/1/1. PUI-B: Prepolymerization at 60°C for 0.5 h, MDI/DEG/PMDA = 2/1/1.

tion time was 1.5–2.0 h for the polyurethane prepolymer procedure and 3.0–3.5 h for the polyimide prepolymer procedure. Also, polymers prepared according to Scheme 2 had relatively higher inherent viscosities than polymers prepared according to Scheme 1. The dependence of the polymer inherent viscosity on the polymerization procedure can be attributed to the different reactive abilities of the groups. The different solubilities of polyurethane and polyimide prepolymers may also be a reason. According to Figure 2, PUI prepared according to Scheme 1 had a maximum inherent viscosity of 0.37 g/dL, and the inherent viscosity remained constant after an approximately 12 h chain-extending reaction. However, for Scheme 2 the optimum chain-extending reaction time was about 20 h, and the resulting polymer had a higher inherent viscosity compared than that from Scheme 1. Another experiment result that should be taken into consideration is that prolonging the chain-extending reaction time continuously after 24 h led to a slight decrease in the polymer inherent viscosity. The reason for this decrease may be the generation of

carboxylic groups from the side reaction of anhydrides with urethane groups or moisture. It has been found that the existence of carboxylic group will decrease the viscosity of PUI.¹⁶

To restrain the side reaction of anhydrides with urethane groups during the chain-extending reaction, we adopted a two-step chain-extending procedure involving a reaction at room temperature followed by a reaction at 80°C, and the results are given in Table II. Obviously, a two-step chain-extending reaction procedure can increase the inherent viscosity of the resulting polymer. A reasonable explanation for the apparent increase should consider the reaction mechanism of isocyanates and anhydrides, on which a great deal of research has been done. It is commonly accepted that there is an intermediate of seven member rings between the reaction components and the imide compound.¹⁸ Therefore, Scheme 2 should be expressed in the detailed form of Scheme 4 when a chain-extending reaction is carried out at first at room temperature.

In Scheme 4, the PUI main chain not only consists of benzene rings and imide rings but also

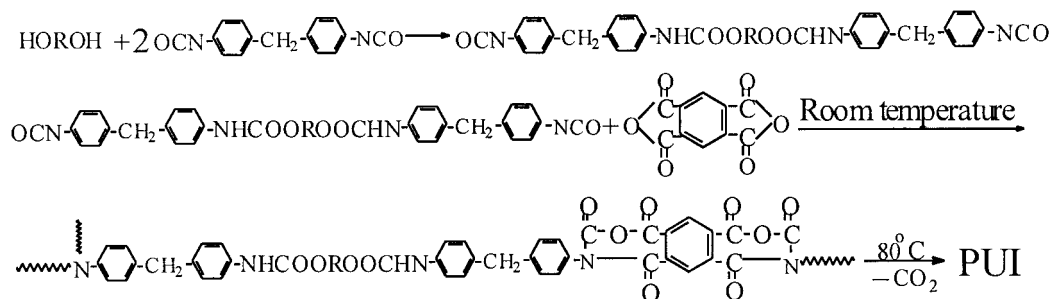
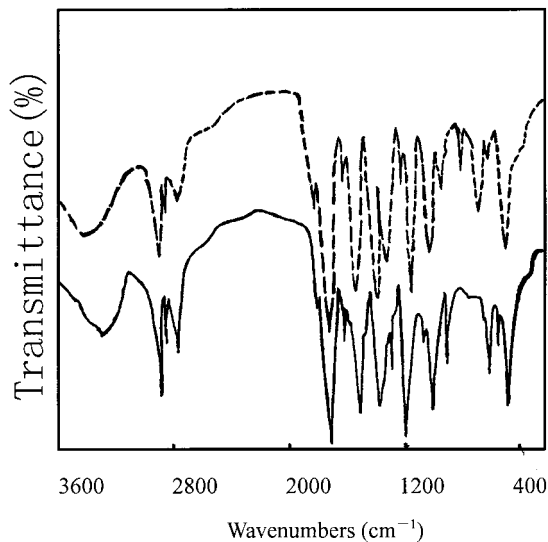

Scheme 4 Synthetic reaction mechanism of PUI from polyurethane prepolymer.

Table III Yield, Inherent Viscosity and Elemental Analysis Results of Poly(urethane-imide) from Polyurethane Prepolymer

	Elemental Analysis (%)												
	PMDA (mol)		HO—R—OH (mol)		MDI (mol)		Prepolymerization (°C, h)		Yield (%)		Inherent Viscosity (dl/g)		
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	
PUI-1	1	2	2	3	80, 2.5	75.6	0.87	74.98	74.55	4.69	4.79	6.23	6.29
PUI-2	1	1	1	2	80, 2.0	77.8	0.86	74.81	74.13	4.27	4.43	6.27	6.53
PUI-3	2	1	1	3	80, 1.5	66.2	0.83	74.10	73.67	3.98	4.04	6.71	6.79
PUI-4	1	2	2	3	60, 0.5	90.3	0.99	70.12	69.89	4.01	3.94	7.59	7.53
PUI-5	1	1	1	2	60, 0.5	87.2	0.98	70.12	68.48	4.12	4.35	7.07	7.61
PUI-6	2	1	1	3	60, 0.5	88.7	0.99	67.77	67.03	4.84	4.76	7.58	7.69

PUI-1,2,3: HO—R—OH = BHPP; PUI-4,5,6: HO—R—OH = DEG. Chain-extending reaction: 4 h at room temperature then 20 h at 80°C.

**Figure 3** FTIR spectra of (—) PUI-1 and (---) PUI-4.

possesses extremely high symmetry. Therefore, the solubility of the polymerization system will be limited, even if it is homogeneous all the time. However, when the chain-extending reaction is carried out at first at room temperature, the symmetry of the intermediate polymer main chain should decrease to a great degree. Therefore, the solubility of the polymerization system should be improved. In addition to the contribution of improved solubility to the increased polymer viscosity, a more important reason should be the restraint of side reactions at room temperature, especially the reaction of anhydride with urethane groups. As confirmed in model reaction studies, the reaction of anhydrides with urethane groups can go forward at a certain speed at 80°C.

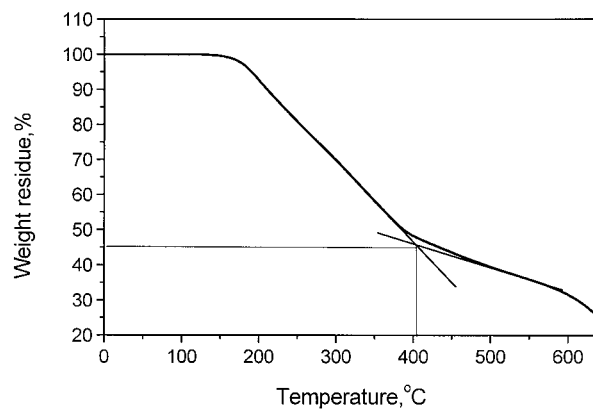
**Figure 4** Typical TGA trace of PUI (in air at 10°C/min).

Table IV Solubility Behavior and Film Properties of Poly(urethane-imide)

Polymer Symbol	Solubility in Different Solvent								Film Properties	
	NMP	DMAc	DMF	THF	DCM	Toluene	Acetone	Hexane	Appearance	Flexibility
PUI-1	++	++	++	±	±	±	—	—	Brown and transparent	Flexible
PUI-2	++	++	++	±	±	—	—	—	Brown and transparent	Flexible
PUI-3	++	++	++	±	±	—	—	—	Brown and transparent	Flexible
PUI-4	++	++	++	+	+	±	—	—	Brown and transparent	Flexible
PUI-5	++	++	++	+	±	±	—	—	Brown and transparent	Flexible
PUI-6	++	++	++	±	±	±	—	—	Brown and transparent	Flexible

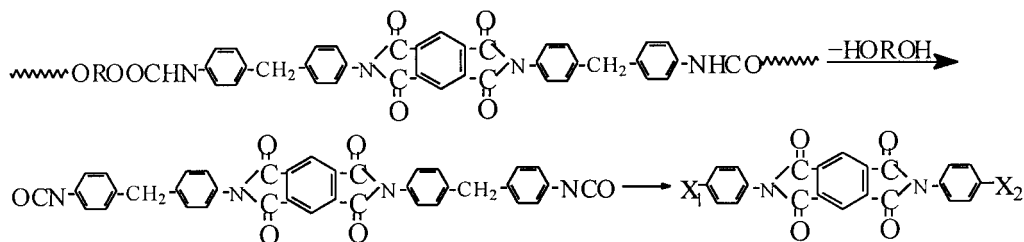
Films were cast by slow evaporation of polymer in NMP. ++: soluble, +: partial soluble; ±: swelling; —: insoluble.

On the one hand, the side reaction of anhydrides with urethane groups will consume excess anhydride, so the functional groups will no longer be equivalent. On the other hand, the side reaction of anhydrides with urethane groups will generate hydroxyl groups, and the hydroxyl groups will react again with anhydrides to consume more anhydrides and form carboxylic groups, which will lead to decrease polymer inherent viscosity.¹⁶ Therefore, it can be concluded that it is most important to restrain the side reaction of anhydrides with urethane groups in the preparation of PUI with a high inherent viscosity. Based on studies of the synthesis procedure and technology, six kinds of PUIs with different ratios of imide to urethane were prepared, and the experimental results are summarized in Table III. All the six PUIs possessed relatively high inherent viscosities. At the same equivalent ratio of imide to urethane groups, PUI from DEG had a higher inherent viscosity than PUI from BHPP. Figure 3 provides IR spectra of PUI-1 and PUI-4. The inherent peaks at 1780 and 1725 cm^{-1} prove the existence of imide and urethane structures, and the other four kinds of PUIs had IR spectra similar to the spectrum of PUI-1 or PUI-4. Results in Table IV indicate all six kinds of PUIs not only

had improved solubility in organic solvents but also could form flexible and transparent films because of their relatively high inherent viscosity.

Thermal Properties of PUI

Figure 4 presents a typical TGA curve of PUI. Similar to Hasmukh and Hemant's experimental results,¹⁵ all six kinds of PUIs exhibited a two-step thermal weight-loss pattern. The linking groups were imide rings, methylene, and isopropylidene and urethane groups between benzene rings in the PUI main chain. In general, imide rings are considered to be the most stable units among these linking groups, followed by methylene and isopropylidene, but urethane groups must be the most labile units and will decompose first to start the initial thermal degradation. It is also commonly accepted that polyurethane undergoes main-chain scission to form isocyanate and hydroxy compounds.^{19,20} On the basis of the structure of PUI, an acceptable degradation procedure of the first step is roughly expressed in Scheme 5. It must be emphasized here that the terminal groups of the final fragment in Scheme 5, X_1 and X_2 , may be —H, —COOH, or —OH. To simplify the following calculation, we considered



Scheme 5 Thermal degradation procedure of PUI at the first step of thermal degradation.

Table V TGA Analysis of PUI (Air, 10°C/min)

	T_i	T_5	T_{30}	T_{st}	$W_{1.TGA}$	$W_{1.th}$
PUI-1	178	192	278	199	65.8	72.5
PUI-2	180	188	280	119	50.0	57.1
PUI-3	184	186	305	126	37.4	40.5
PUI-4	228	278	340	154	60.7	66.3
PUI-5	231	272	353	157	42.5	50.0
PUI-6	238	269	371	162	32.1	34.1

T_i : initial weight loss temperature; T_5 , T_{30} : temperature at 5% and 30% weight loss; $T_{st} = 0.49[T_5 + 0.6(T_{30} - T_5)]$, $W_{1.TGA}$ = weight loss percentage at the first weight loss stage.

both X_1 and X_2 to be —H. According to Scheme 5, the possible weight-loss percentage $W_{1.th}$ of the first step of thermal degradation can be calculated. The values of $W_{1.th}$ and the details of the TGA analysis results are detailed in Table V. PUI-1,2,3 had some lower initiated thermal decomposition weight-loss temperatures compared with PUI-4,5,6. All the initial thermal decomposition weight-loss temperatures also rose slightly when the imide content increased in the polymer main chain. However, the temperature at 5% weight loss was different from the initial weight-loss temperature; this may be due to the incompatibility of imide and urethane groups. In a comparison of $W_{1.th}$ and $W_{1.TGA}$, all the calculated values are slightly higher than the measured values. The deviation should have resulted for the following two reasons. First, $W_{1.th}$ was calculated according to Scheme 5. As emphasized previously, the terminal groups of the final fragment, X_1 and X_2 , are considered to be —H. In fact, they may be

—H, —COOH, or —OH. Therefore, the calculated results will be higher than the measured values. Second, the evaporation hysteresis of the evaporable decomposition products will also give rise to the deviation between $W_{1.th}$ and $W_{1.TGA}$. Although there is deviation between $W_{1.th}$ and $W_{1.TGA}$, $W_{1.th}$ can still be thought to coincide with $W_{1.TGA}$ to some degree.

For more proofs to understand the thermal degradation process of PUI, the effect of thermal treatments on the polymer inherent viscosity and polymer film properties was investigated. The solubility of the residues at the end of the first step of thermal degradation was also taken into consideration. As summarized in Table VI, the sharp decrease in the polymer inherent viscosity provides evidence for depolycondensation during the first step. Furthermore, all these polymer films became brittle because of the scission of the backbone. Because of the poor solubility of imide compounds, as confirmed in model reaction studies, the residues showed only slight solubility in organic solvents such as DMF, DMAc, and NMP. This implied that the residues at the end of the first step of thermal degradation were imide compounds. These results confirm the view that the first step of thermal degradation of PUI is due to depolycondensation of all the urethane units and scission of the others linkage groups of the PUI main chain, except for imide rings.

CONCLUSIONS

Six kinds of thermoplastic PUIs with high inherent viscosities were prepared on the basis of de-

Table VI Effect of Thermal Treatment on the Inherent Viscosity of PUI

Condition of Treatment (°C, h)	Inherent Viscosity (dL/g)		Film Properties		Solubility of the Residues at the End of the First Step ^a	
	Before	After	Before	After		
PUI-1	170,1	0.87	0.20	Flexible	Brittle	Poor
PUI-2	170,1	0.86	0.23	Flexible	Brittle	Poor
PUI-3	170,1	0.83	0.27	Flexible	Brittle	Poor
PUI-4	170,1	0.99	0.94	Flexible	Flexible	Poor
PUI-4	210,1	0.99	0.36	Flexible	Brittle	Poor
PUI-5	170,1	0.98	0.96	Flexible	Flexible	Poor
PUI-5	210,1	0.98	0.34	Flexible	Brittle	Poor
PUI-6	170,1	0.99	0.97	Flexible	Flexible	Poor
PUI-6	210,1	0.99	0.40	Flexible	Brittle	Poor

^a The solvents used were NMP, DMF, and DMAc.

tailed studies of model reactions and synthesis procedures, and they were characterized by elemental analysis and IR measurements. Studies on the synthesis procedure proved that it was most important to restrain the side reaction of anhydrides with urethane groups in the preparation of PUIs with high inherent viscosities. Prepared polymers not only exhibited improved solubility in organic solvents but also formed flexible and transparent films. TGA analysis showed that all the six PUIs exhibited a two-step thermal decomposition pattern. The first-stage weight loss came from the depolycondensation of urethane groups and the scission of the other linkages, except for imide rings. During main-chain scission, the polymer inherent viscosity decreased sharply, and polymer films were no longer tough and flexible. Based on the structures of the PUIs and an understanding of the degradation mechanism of polyurethane, the possible weight-loss percentage at the end of the first step of thermal degradation was calculated. There was a satisfactory coincidence between the calculated weight-loss percentage and the measured value.

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